Chemosphere 198 (2018) 274–280

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

An improved method for determining dermal exposure to polycyclic aromatic hydrocarbons

Bo Strandberg [a, e, *], Anneli Julander [b], Mattias Sjöström [c, d], Marie Lewné [c, d], Hatice Koca Akdeva[e], Carolina Bigert [c, d]

[a] Division of Occupational and Environmental Medicine, Lund University, Lund, Sweden
[b] Unit of Work Environment Toxicology, Institute of Environmental Medicine, Karolinska Institutet, Stockholm, Sweden
[c] Unit of Occupational Medicine, Institute of Environmental Medicine, Karolinska Institutet, Stockholm, Sweden
[d] Centre for Occupational and Environmental Medicine, Stockholm County Council, Stockholm, Sweden
[e] Section of Occupational and Environmental Medicine, Institute of Medicine, Sahlgrenska Academy at the University of Gothenburg, Gothenburg, Sweden

HIGHLIGHTS

- The procedure can clean-up tape-strips to assess dermal exposure to multiple PAHs.
- The procedure is simple, non-destructive and gives clean extracts for GC/MS analysis.
- The method can be used in working exposure situations and in the general population.
- Both gaseous and particle-bound PAHs, including alkylated species, could be detected.

ARTICLE INFO

Article history:
Received 27 September 2017
Received in revised form
11 January 2018
Accepted 22 January 2018

Handling Editor: Andreas Sjodin

Keywords:
Semipermeable membranes
PAHs
Dermal exposure
Tape-strips

ABSTRACT

Many workers are occupationally exposed to polycyclic aromatic hydrocarbons (PAHs), which may cause various health problems, and some PAHs are known or suspected carcinogens. PAH exposure is primarily monitored by air sampling, but contamination may also occur through dermal exposure. PAHs adsorbed to the skin can be sampled by tape-stripping, but subsequent extraction of sampling tapes in organic solvent also releases diverse co-eluting substances that are difficult to remove before analysis of the PAHs by gas chromatography/mass spectrometry (GC/MS). The objective of this study was to optimise a procedure for analytical clean-up after extraction of 32 PAHs from tape-strips, by dialysis in organic solvent using semipermeable membranes. With triplicate subsamples, the developed method yields acceptable precision and repeatability for both the 32 PAHs, across the concentration range 10–160 ng per sample, and for a certified reference material (urban dust). The optimized clean-up procedure and GC/MS methodology was used to assess PAHs on skin from the lower part of the ventral side of the wrist and just below the collar bone of three firefighters and seven controls (office workers). Several gaseous and particle-bound PAHs were detected in all samples, including controls. Thus, the optimized procedure using semipermeable membranes for clean-up of tape-strip extracts can be used to assess the dermal exposure of both occupational and general populations to multiple PAHs. The results also show that both gaseous and particle-bound PAHs, including alkylated species, may be present on skin.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are substances characterized by the presence of two or more benzene rings. They are naturally occurring compounds, but can also be formed by incomplete combustion of organic material or during various industrial processes. Many PAHs are known or suspected carcinogens (Boström et al., 2002; IARC, 2016). There are indications that compounds other than the known carcinogenic native PAHs, e.g. alkylated PAHs, contribute to PAH toxicity (Van Rooij and Jongeneelen, 2007) and thus should be included in PAH exposure studies.

* Corresponding author. Division of Occupational and Environmental Medicine, Lund University, Lund, Sweden.
E-mail address: bo.strandberg@med.lu.se (B. Strandberg).

https://doi.org/10.1016/j.chemosphere.2018.01.104

Humans may be exposed to PAHs from diverse sources via several routes, such as ingestion of contaminated food or water, inhalation of contaminated air and dermal contact. Occupational exposure to PAHs may occur mainly via inhalation and dermal exposure. Some studies even indicate that dermal exposure might have greater impact than inhalation exposure (Van Rooij et al., 1993a, b; Borak et al., 2002; Sartorelli, 2002).

Exposed occupational groups include (for example) coke plant workers, aluminium production workers, chimney sweeps, roofers and asphalt workers (IARC, 2010a; Driscoll et al., 2016), professional drivers (IARC, 2014), kitchen workers (IARC, 2010b; Ke et al., 2016; Lewné et al., 2017) and firefighters (IARC, 2010c; Fent et al., 2014).

To evaluate dermal exposure to chemicals several types of methods may be used, generally called removal, surrogate skin or fluorescent tracer techniques (Brouwer et al., 2000). The most suitable approach depends on the nature of the targeted chemicals. Two widely applied techniques, involving sampling using appropriate skin wipes or hand-washing, have been used to assess occupational exposure to diverse compounds, including pesticides, metals, hair dyes, and PAHs (Fenske, 1993; Brouwer et al., 2000; Julander et al., 2010). A relatively new methodology to assess dermal exposure to various compounds in occupational situations is tape-stripping (Nylander-French, 2000; Mattorano et al., 2004; Chao et al., 2005; Liljelind et al., 2007, 2010; Eriksson et al., 2008). Recently Kammer et al. (2011) evaluated the method for measuring dermal exposure to two PAHs, pyrene and benzo(a) pyrene, and showed that chimney sweeps' skin was contaminated by these chemicals.

Irrespectively of the method used to sample skin, appropriate procedures must be applied to ensure that the sample is sufficiently clean for the subsequent analysis. Thus, the sampling, extraction and analytical purification methods used to assess dermal exposure to PAHs must not damage either subjects' skin or the collected samples. However, diverse co-eluting substances are released during the extraction of tape-strips, which complicates analysis of trace contaminants, such as PAHs. Thus, clean-up procedures are crucial elements of any analysis of trace organic pollutants in such samples, and several methods have been developed to clean-up samples of biological materials and other complex matrixes that are difficult to clean using traditional approaches. These include destructive methods, such as sulphuric acid treatment, and non-destructive methods such as gel permeation chromatography or dialysis with organic solvent using semipermeable low-density polyethylene membranes (hereafter SPMs, for convenience) (Strandberg et al., 1998; Bergqvist et al., 1999; Rantalainen et al., 2000; Wenzel et al., 2004). The optimal analytical methodology should ideally be simple, non-destructive and efficient, without using excessive solvents, yielding clean extracts that are suitable for analysis by gas chromatographic mass spectrometry (GC/MS).

The objective of this study was to evaluate the utility of SPM methodology, and optimise it, for analytical purification after extraction of tapes used to sample multiple PAHs on the skin of exposed workers. The assessments included analysis of samples of both tapes spiked with standards and, in a field pilot study, tapes used to sample substances on the skin of firefighters and a set of controls (office workers). The following sections report the analyses and results in terms of: internal standard recoveries; the precision, repeatability and accuracy of measurements of the studied compounds; and amounts of PAHs detected on the skin of the two occupational groups.

2. Material and methods

The SPMs used in the study were made from a single "layflat" low density polyethylene dialysis tube, 26 mm wide and 80 μm thick (ExposMeter AB, Umeå, Sweden), which was cut to appropriate lengths (about 250 mm) and heat-sealed at one end. All adsorbents, silica gel 60 (Merck, Darmstadt, Germany), aluminium oxide 90 active neutral (Merck, Darmstadt, Germany), and sodium sulfate (Merck, Darmstadt, Germany) were cleaned by thermal treatment at 450 °C and activated at 100 °C before use. An internal standard mixture (1 ng μL^{-1}) containing the 16 deuterated U.S. Environmental Protection Agency (USEPA) priority PAHs and a native PAH mix containing the 16 USEPA PAHs plus 16 alkylated species, all at 1 ng μL^{-1} (Table 1), were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The standard reference material 1649a (urban dust) was purchased from the US National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). All solvents used were of glass-distilled quality (Sigma Aldrich, St Louis, MO, USA). All glassware (beakers, vials, Pasteur pipettes etc.) were cleaned by thermal treatment at 450 °C before use.

2.1. Tape-stripping method

The tape-stripping technique is based on the assumption that uptake of a chemical through the skin can be traced by repeatedly placing strips of a suitable tape on the same surface area, removing them and then measuring the amount of the chemical in each tape. However, this is only strictly true if more than 20–30 tapes are used and a glistening wound is visible on the skin area after taping (Hostynek et al., 2001). In occupational exposure studies 3–5 tapes are routinely used. This has been shown to provide good surface samples, but does not indicate uptake through skin.

The tape-strips used here were pre-cut in 3×5 cm^2 portions of Fixomull adhesive tape (BSN medical GmbH & Co, Hamburg, Germany). The strips used for the laboratory experiments were cut and immediately used. Three tapes were used for each sample, to mimic skin sampling. Three blank tapes were also collected on each sampling (laboratory or field) occasion. Each set of three tapes, sample or blank, was pooled for subsequent analysis.

In the field study, we used the tape-stripping method described by Kammer et al. (2011) with some modifications. Briefly, the tape-strips were kept in clean Petri dishes in a bag to minimize risk of contamination before use. Samples were taken from the surface of skin on the lower part of the ventral side of the wrist and just below the collar bone. The tapes were applied with fingertip pressure to the targeted surface area of the exposed skin. The corners of the tape were indicated with a marker pen to indicate the sampled surface area. After 2 min of adhesion the tape was slowly removed, at an angle of about 45°. The tape was then folded to ensure that the sticky side of the tape did not come into contact with anything else. Three consecutive tapes were used to sample each selected surface area. After removal, all three tapes were placed in a Petri dish, wrapped in alumina foil and stored at −20 °C prior to analysis.

2.2. Sample extraction

Each set of three tape-strips was placed in a 10 mL amber glass scintillation vial. A 40 μL portion of the deuterated PAH internal standard mixture was added, then the strips were extracted in 5 mL of dichloromethane by agitation in a Sonica ultrasonic extractor (Soltec, Milan, Italy) for 30 min. The resulting extract was quantitatively transferred to a 25 mL amber glass vial. The extraction procedure was repeated twice, and the pooled extracts from each set of samples were combined and evaporated to approximately 5 mL by purging with nitrogen. The analytes were then transferred to n-hexane, solvent exchanged in 2×2 mL of n-hexane, which was further reduced, by evaporation, to a final volume of 2 mL.